The role of mineral structure in metal speciation and cycling in contamined soils

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1 Introduction

The birnessite-group minerals with hexagonal layer symmetry are the dominant Mn oxides found in nature. Nano-sized birnessites have a large external and internal surface area and an overall net negative surface potential in the normal pH window; therefore, they possess a high adsorption capacity and affinity for metal ions and are known as a metal scavenger in spite of the much smaller amounts of birnessites than iron and aluminum (hydr)oxides in the subsurface. The developed CD-MUSIC model with mostly predicted parameters based on the birnessite structure and an EDL model composed of a SGC double layer for the external surface and a Donnan phase for the interlayer surface allows a quantitative evaluation of the metal ion adsorption capacity and affinity for both the external and internal surface sites of birnessites. It is helpful to understand better the difference in adsorption mechanism between birnessite and iron and aluminum (hydr)oxides.

2 Materials and methods

- High-resolution XRD and Rietveld Refinement for birnessite structure with different Mn average oxidation state (MnAOS)
- Pb adsorption experiments, including isotherm and Pb-edge adsorption
- CD-MUSIC-EDL modeling was carried out with PEST-ORCHESTRA, our CD-MUSIC-EDL model comprises of an EDL model and a CD-MUSIC part as shown in the conceptual model in Figure 1

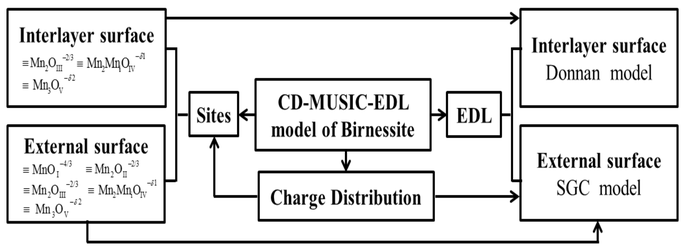

Figure 1 Conceptual model for CD-MUSIC-EDL model for birnessites.

3 Results

3.1 Birnessite surface sites and densities

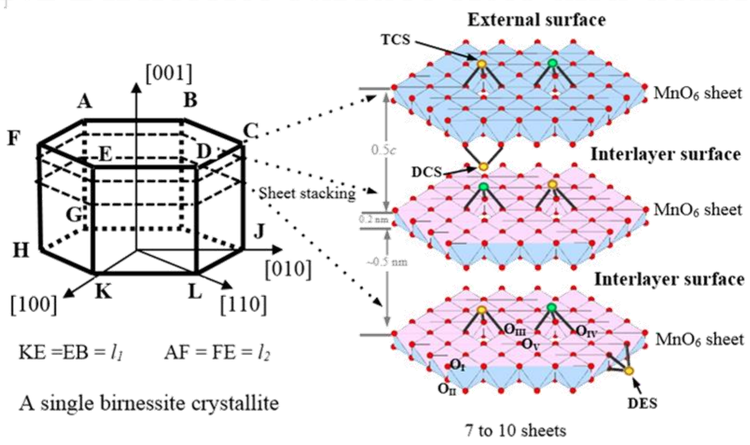

Figure 2 Schematic view of the different surface groups and the three stable surface complexes of Pb^{2+} on birnessite.

There are 7-10 MnO_6 layer sheets in a single birnessite crystallite, and a total of 9-12 Mn atoms are present at each edge of the hexagon MnO_6 layer sheet.

Table 1 site densities of the different surface groups of the birnessites

Sample	external surface (CD-MUSIC-SGC model)						
	A_1 (nm^2)	$A_{ES\ total}$ ($m^2\ g^{-1}$)	$N_{1,\equiv MnO_I^{-4/3}}$ (mol kg^{-1})	$N_{1,\equiv Mn_2O_{II}^{-2/3}}$ (mol kg^{-1})	$N_{1,\equiv Mn_2O_{III}^{-2/3}}$ (mol kg^{-1})	$N_{1,\equiv Mn_2Mn_IO_{IV}^{-\delta 1}}$ (mol kg^{-1})	$N_{1,\equiv Mn_3O_V^{-\delta 2}}$ (mol kg^{-1})
HB1	59	235	2.5	2.2	1.2	0.3	1.0
HB2	64	176	2.2	2.0	0.9	0.6	0.8
HB3	101	151	1.8	1.6	0.7	0.7	0.4
	interlayer surface (MUSIC-Donnan model)						
	A_2 (nm^2)	$A_{IS\ total}$ ($m^2\ g^{-1}$)	$N_{2,\equiv Mn_2O_{III}^{-2/3}}$ (mol kg^{-1})	$N_{2,\equiv Mn_2Mn_IO_{IV}^{-\delta 1}}$ (mol kg^{-1})	$N_{2,\equiv Mn_3O_V^{-\delta 2}}$ (mol kg^{-1})	Donnan volume ($L\ kg^{-1}$)	Initial surface charge (mol kg^{-1})
HB1	219	875	7.1	2.0	6.2	0.23	-1.51
HB2	265	729	6.0	4.3	5.3	0.19	-1.37
HB3	541	809	5.8	6.6	3.8	0.21	-1.22

3.2. Proton affinity constants

Table 2 Proton affinity constants of the surface groups

Sample (MnAOS)	Group	logK_H(oxo)	logK_H(hydroxo)
HB1 (3.92)	$\equiv MnO_I^{-4/3}$	16.5	4.7
	$\equiv Mn_2O_{II,III}^{-2/3}$	1.4	-10.5
	$\equiv Mn_2Mn_IO_{IV}^{-\delta 1}$	-2.5	-
	$\equiv Mn_3O_V^{-\delta 2}$	-9.8	-
HB2 (3.83)	$\equiv MnO_I^{-4/3}$	16.5	4.6
	$\equiv Mn_2O_{II,III}^{-2/3}$	1.2	-10.6
	$\equiv Mn_2Mn_IO_{IV}^{-\delta 1}$	-2.9	-
	$\equiv Mn_3O_V^{-\delta 2}$	-10.0	-
HB3 (3.67)	$\equiv MnO_I^{-4/3}$	16.0	4.1
	$\equiv Mn_2O_{II,III}^{-2/3}$	0.3	-11.6
	$\equiv Mn_2Mn_IO_{IV}^{-\delta 1}$	-3.4	-
	$\equiv Mn_3O_V^{-\delta 2}$	-11.4	-

With the predicted logK_H values of the coordinated oxygen groups and their site fractions the pH of the point of zero net proton charge or pH_{PZNPC} of the birnessite samples was predicted with CD-MUSIC-EDL model and are around 2.5, 2.8, and 1.9 For HB1, HB2, and HB3, respectively.

Table 3 Charge distribution (CD) values of Pb surface complexes at the external surface

Pb complex on surface	$\Delta z_0 / \Delta z_1$	log$K$(Pb)	
DCS:	0.67/1.33	HB1	10.9
$2\equiv MnO_IH^{-1/3} + Pb^{2+} \rightleftharpoons [\equiv (MnO_IH)_2 - Pb]^{+4/3}$		HB2	8.9
		HB3	8.2
DES:	1.06/0.94	HB1	6.9
$2 \equiv MnO_IH^{-1/3} + \equiv Mn_2O_{II}^{-2/3} + Pb^{2+} \rightleftharpoons [\equiv Mn_2O_{II} - Pb - (\equiv MnO_IH)_2]^{+2/3}$		HB2	8.3
		HB3	7.4
TCS (vacant sites)	1.17/0.83	HB1	6.5
$3 \equiv Mn_2O_{III}^{-2/3} + Pb^{2+} \rightleftharpoons [\equiv (Mn_2O_{III})_3 - Pb]^0$		HB2	6.1
		HB3	2.2

The logK_{Pb} values reveal that the Pb binding constants for the DCS, DES, and TCS complexes tend to decrease with decreasing MnAOS. Moreover, logK_{Pb}(DCS) > logK_{Pb}(DES), which may be due to a steric effect.

3.3. Modeling results of Pb adsorption

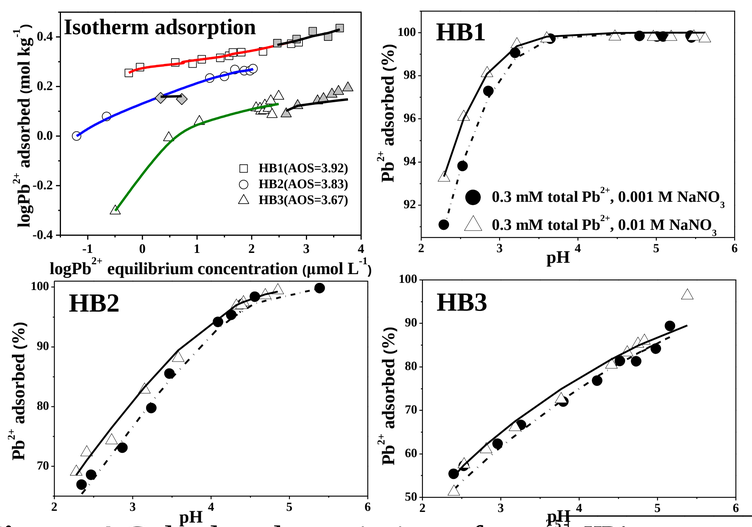

Figure 3 Adsorption experiments of Pb^{2+} to birnessites.

For all HB samples a good description of the Pb adsorption (R^2 > 0.993) is found, see Figure 3. Also the Pb adsorption on birnessites reported by the literature can be described well.

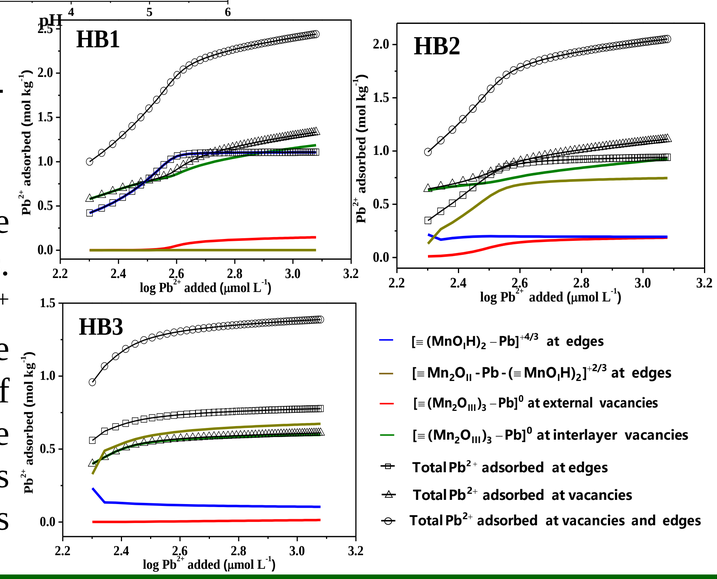

Figure 4 Calculated speciation of Pb complexes according to the CD-MUSIC-EDL model with the fitted Pb binding constants.

with decreasing MnAOS the contribution of edge sites increases. Though at high Pb added Pb^{2+} adsorbed predominantly on the external surface, the contribution of the interlayer surface is quite significant. And much more Pb^{2+} is adsorbed on the internal vacancies than on the external vacancies.

4 Conclusions

- The larger logK_{Pb} value was obtained for higher MnAOS;
- with increasing MnAOS the interlayer surface contribution to the total Pb^{2+} adsorption increased, and the vacancy contribution increased. The vacancy contribution from interlayer surface was predominant.

5 References

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